



Subcomponent Flexibility Enables Conversion between D_4 -Symmetric $\text{Cd}^{\text{II}}_8\text{L}_8$ and T -Symmetric $\text{Cd}^{\text{II}}_4\text{L}_4$ Assemblies

Jesús Mosquera, Tanya K. Ronson, and Jonathan R. Nitschke*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

S Supporting Information

ABSTRACT: A flexible tris-formylpyridine subcomponent **A** was observed to produce three distinct products following Cd^{II} -templated self-assembly with different anilines. Two of the products were $\text{Cd}^{\text{II}}_4\text{L}_4$ tetrahedra, one with ligands puckered inward, and the other outward. The third product was a $\text{Cd}^{\text{II}}_8\text{L}_8$ structure having all *mer* stereochemistry, contrasting with the *fac* stereochemistry of the tetrahedra. These three complexes were observed to coexist in solution. The equilibrium between them could be influenced through guest binding and specific interactions between aniline subcomponents, allowing a selected one of the three to predominate under defined conditions.

Subcomponent self-assembly is a powerful tool for the construction of increasingly complex metallo-supramolecular architectures.¹ This technique generates dynamic coordinative ($\text{N} \rightarrow \text{metal}$) and covalent ($\text{N}=\text{C}$) bonds during a single overall process.² Metal–organic polyhedral complexes obtained with this strategy have proven useful in a wide range of different applications, including guest sequestration,³ biological activity,⁴ molecular sensing,⁵ and gas separation.⁶ Much understanding has been gained in recent years as to the design principles governing the construction of metal–organic architectures,⁷ feeding back into the design of new structures with targeted functions.⁸

The design principles uncovered so far have been used principally to build rigid ligands that possess the correct geometry for the desired product structure. Although the use of rigid ligands in self-assembly has provided access to many functional supramolecular architectures,^{2,9} more flexible ligands may adopt conformations that enable the attainment of even greater structural complexity, as exemplified by work from the Ward group.¹⁰

The use of flexible ligands in self-assembly presents two challenges: different ligand conformations can allow multiple assemblies to form simultaneously, and flexible ligands may chelate metal ions instead of bridging between them, generating entropically favored small assemblies that lack cavities.^{1b,11} If the right balance is struck between flexibility and rigidity, however, a limited number of assemblies may be formed, and the ratio between them might be controlled under different conditions.^{10d,12} Through understanding how to deploy the degrees of freedom of flexible ligands, new structure types may be obtained, which might not be accessible using rigid ligands.^{10f,13}

Here we describe a system based on flexible subcomponent **A** (Scheme 1), which reacts with *p*-toluidine and Zn^{II} or Cd^{II} to generate a dynamic library of three distinct self-assembled structures in solution. The equilibrium between these structures is influenced by different templation effects. One product has an unprecedented architecture, comprising eight tritopic organic ligands and eight *meridional*- Cd^{II} centers.

Subcomponent **A** (Scheme 1) was prepared in one step from commercially available starting materials as described in the Supporting Information (SI). The reaction of **A** (1 equiv) with $\text{Zn}(\text{OTf})_2$ (1 equiv) and *p*-toluidine (3 equiv) in acetonitrile gave a single product (**1**, *exo*- Zn_4L_4 , Scheme 1, (i)) as confirmed by ^1H NMR spectroscopy (Figure S3) and mass spectrometry (Figure S10). X-ray crystallography provided a solid-state structure (Figure 1) consistent with solution measurements.

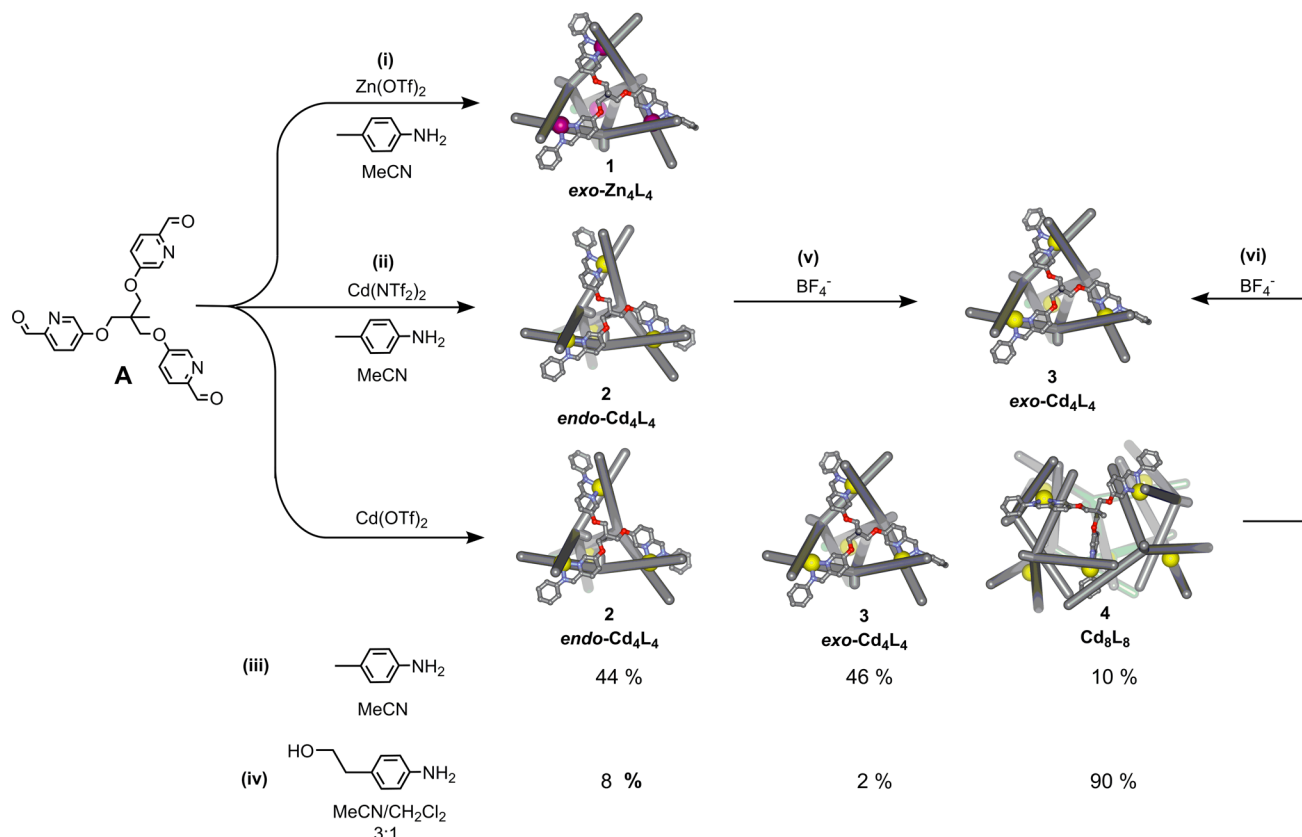
Complex **1** consists of a tetrahedral arrangement of four *facially* coordinated octahedral Zn^{II} centers bridged by four tritopic ligands, each of which caps a face of the tetrahedron. The ligands on the faces adopt a C_3 -symmetric propeller-like configuration, and the methyl groups of **A** point outward, away from the cavity. The zinc(II) centers are separated by an average of 11.9 Å, and the volume of the central cavity was measured to be 194 Å³ (SI section 5). A disordered triflate anion is encapsulated within the cavity, which can be replaced by BF_4^- or PF_6^- through anion metathesis.

When the same procedure was carried out using $\text{Cd}(\text{OTf})_2$ in place of $\text{Zn}(\text{OTf})_2$ (Scheme 1, (iii)), ^1H NMR identified the formation of three different complexes: 44% of the ligand **L** was incorporated into complex **2** (which we infer to be *endo*- $\text{Cd}^{\text{II}}_4\text{L}_4$; see below), 46% into **3** (*exo*- $\text{Cd}^{\text{II}}_4\text{L}_4$) and 10% into **4** ($\text{Cd}^{\text{II}}_8\text{L}_8$) (Figure S25), where **L** is the tris(pyridylimine) ligand derived from condensation of **A** with 3 equiv of *p*-toluidine. Whereas **2** and **3** displayed a single set of resonances for each ligand environment, consistent with *T* symmetry, in the case of **4** three sets of resonances in a 1:1:1 ratio were observed, which is typical of lower-symmetry *meridional* (*mer*) coordination. Diffusion-ordered NMR spectroscopy (DOSY) indicated that **2** and **3** are of similar size (diffusion coefficient of $4.2 \times 10^{-10} \text{ m}^2/\text{s}$), whereas **4** is larger, with a diffusion coefficient of $3.1 \times 10^{-10} \text{ m}^2/\text{s}$. Peaks corresponding to both $\text{Cd}^{\text{II}}_4\text{L}_4$ and $\text{Cd}^{\text{II}}_8\text{L}_8$ were observed by mass spectrometry (Figures S34–S36).

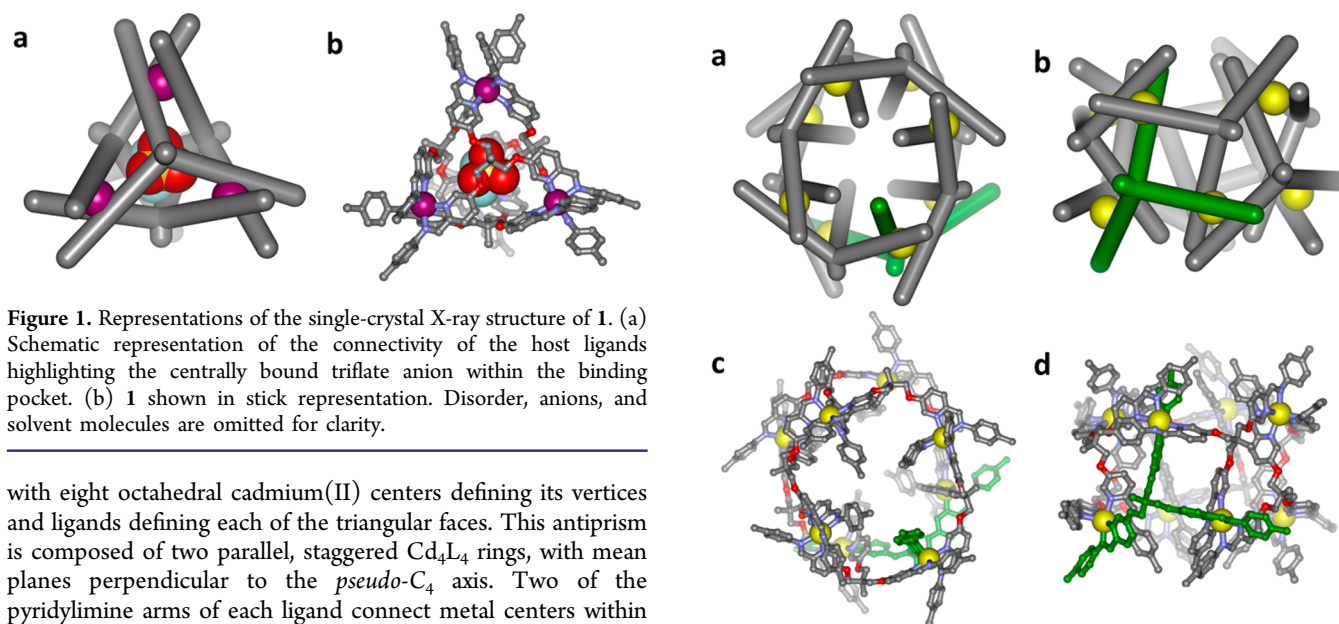
The X-ray crystal structure of **4** revealed a new type of $\text{Cd}^{\text{II}}_8\text{L}_8$ assembly with approximate D_4 point symmetry (Figure 2). The structure can be described as a tetragonal antiprism,

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Scheme 1. Syntheses and Schematic Representations of Architectures 1–4 Obtained from Subcomponent A^a

^aApproximate percentages correspond to the amount of total ligand present in the system that is incorporated into each structure. (i–iii) The tetrahedral product noted was generated from the corresponding metal salt, A, and *p*-toluidine (1:1:3). (iv) Cd_8L_8 **4** predominated following the reaction of $\text{Cd}(\text{OTf})_2$, A, and 4-aminophenethyl alcohol (1:1:3). The addition of BF_4^- as a template resulted in the conversion of either (v) $\text{endo-Cd}_4\text{L}_4$ **2** or (vi) Cd_8L_8 **4** into $\text{exo-Cd}_4\text{L}_4$ **3**.



with eight octahedral cadmium(II) centers defining its vertices and ligands defining each of the triangular faces. This antiprism is composed of two parallel, staggered Cd_4L_4 rings, with mean planes perpendicular to the *pseudo-C*₄ axis. Two of the pyridylimine arms of each ligand connect metal centers within the same ring, with Cd–Cd distances of 12.1–13.6 Å, while the third arm bridges to a Cd center in the other ring, with Cd–Cd distances of 11.2–13.2 Å. All cadmium centers display *mer* stereochemistry, in contrast to the *fac*-coordination required to define the 3-fold axes of the smaller tetrahedral capsules **1**, **2**, and **3**. All metal centers within each structure have the same Δ or Λ stereochemistry, and both enantiomers of **4** are present in

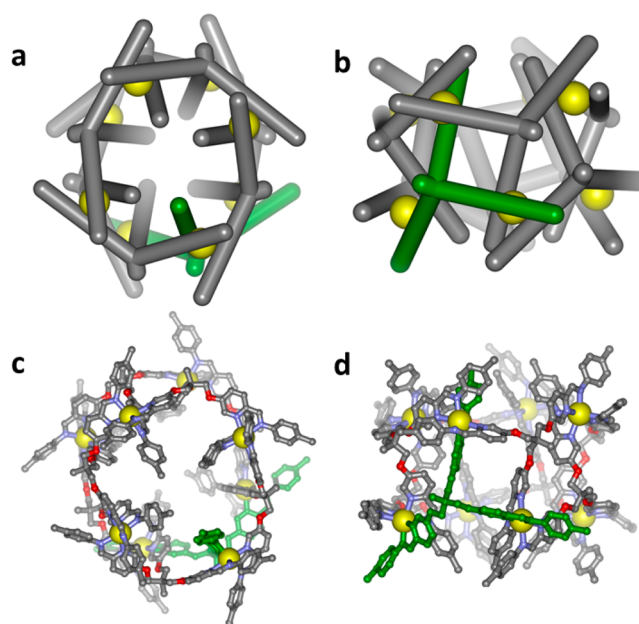


Figure 2. Single-crystal X-ray structure of Cd_8L_8 **4**. (a and b) Schematic views down *pseudo-C*₄ and *pseudo-C*₂ axes, respectively. (c and d) Same views as (a) and (b), but in stick representation. One ligand is shown in green. Disorder, anions, and solvent molecules omitted for clarity.

the unit cell. As in the case of *exo*-Zn^{II}₄L₄ **1**, all of the methyl groups of the **A** residues point outward. The cavity of the complex has a volume of 1050 Å³ (SI section 5), which is partially closed off in the direction of the C₄ axis by the four *p*-toluidines that converge at the “top” and “bottom” faces. Six disordered triflates were found inside the cavity.

The solid-state structure shown in Figure 2 is consistent with the solution NMR data for complex **4**, wherein a tritopic ligand generates a D₄-symmetric assembly in a new way. Its preparation builds upon prior examples of new structure types that can be prepared using multitopic ligands and metal centers of *mer* stereochemistry.¹⁴

Having observed that three distinct products could result from a single set of subcomponents, we sought to understand the factors that favor one over the others. Remarkably, cage **2** was the only product obtained when cadmium(II) bis(trifluoromethane)sulfonimide (triflimide, NTf₂[−]) was used as the template (Scheme 1, (ii)). The addition of BF₄[−] (1 equiv per Cd^{II}) transformed **2** into **3** (Scheme 1, (v)); conversion of the mixture of the three complexes into **3** was also observed following the addition of this template anion (1 equiv per Cd^{II}, Scheme 1, (vi)). The ¹H–¹⁹F HOESY spectrum (Figure S46) showed correlations only between BF₄[−] and the signals of cage **3** in a mixture of **2** and **3**.

Taken together, characterization data for **2** and **3** allow us to infer that both are tetrahedral complexes, which differ only in the orientation of the central CH₃ groups of their ligands. Cage **3** is thus assigned as *exo*-Cd^{II}₄L₄, with all methyl groups pointing outward, resulting in a cavity which can encapsulate TfO[−], BF₄[−], and PF₆[−]. This hypothesis is also supported by the similarity between the ¹H NMR spectra of *exo*-Zn^{II}₄L₄ **1** and *exo*-Cd^{II}₄L₄ **3**. The methyl groups of **2**, in contrast, are inferred to point inward (*endo*-Cd^{II}₄L₄), filling the cavity. Triflimide (volume 157 Å³) would occupy 81% of the cavity of **1** (194 Å³),¹⁵ well above Rebek's optimum of 55% occupation; triflimide is thus too large to be encapsulated by **2**.¹⁶ Hence, when this anion is used as a counterion, we infer that the methyl groups point inward. This configuration avoids the entropic penalty associated with an empty cavity^{10f} and the enthalpic penalty of binding a suboptimal guest, such as acetonitrile or triflimide. Smaller anions, such as BF₄[−], fit inside the cavity and lead to the stabilization of the *exo* configuration. We infer that the lack of observed *endo*-Zn^{II}₄L₄ formation results from the smaller coordination sphere of Zn^{II}, whose stricter geometrical requirements preclude the adoption of a conformation in which the four methyl groups can be accommodated inside the assembly.

The alternative hypothesis that **2** could have the same *exo*-Cd^{II}₄L₄ structure, but with no anion inside, was disfavored by experiments demonstrating that anion exchange within *exo*-Zn^{II}₄L₄ occurred much more rapidly than **2** to **3** interconversion (SI section 4) despite Cd^{II} and Zn^{II} having similar lability.¹⁷

Having solved the crystal structures of Cd^{II}₈L₈ **4** and *exo*-Zn^{II}₄L₄ **1**, we prepared an MM2 model of *endo*-Cd^{II}₄L₄ **2** using CAChe software¹⁸ and compared the conformations of **L** between the different structures. As shown in Figure 3, **L** adopts markedly different conformations in the three assemblies. The major difference between the configurations adopted in *exo*-Zn^{II}₄L₄ **1** (Figure 3, green **L**) and Cd^{II}₈L₈ **4** (red **L**) is that **L** is more splayed open in Cd^{II}₈L₈ **4**, allowing the formation of a larger assembly. Contrary to **1** and **4**, the three anilines in **2** are inferred to point outward, in the same general

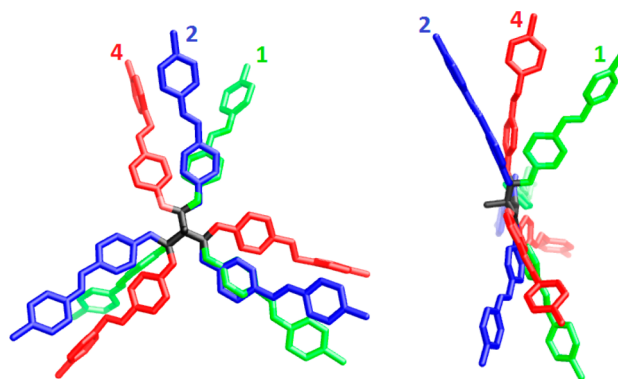


Figure 3. Two views of a superposition of the conformations adopted by **L** within the three complexes **1**, **2**, and **4**, as labeled. The central carbons of **L** used to obtain the superposition are shown in black. Data are taken from X-ray structures for **1** and **4**, and from an MM2 model for **2**.

direction as the central methyl group. The methyl moiety thus remains inside the tetrahedral structure. Comparison of the three distinct ligand conformations in **1**, **2**, and **4** thus strongly implicates the flexibility of **L** in the ability of this system to generate the diversity of structures.

We then explored factors that might favor the formation of Cd^{II}₈L₈ **4**. When self-assembly was carried out at higher concentrations, the proportion of **4** increased, as the entropic penalty diminished for incorporating more subcomponents per assembly. When the concentration was doubled (32 mM of **L**), 36% of **L** was incorporated into complex **4**, 33% into *exo*-Cd^{II}₄L₄ **3**, and 31% into *endo*-Cd^{II}₄L₄ **2**. The use of other solvents (MeOH, hexafluorobenzene, and chloroform), anions (Mo₆O₁₉^{2−}, CB₁₁H₁₂[−], B₁₂F₁₂^{2−}, or B(C₆F₅)₄[−]), and aniline subcomponents (*p*-anisidine, 4-*tert*-butylaniline, and 5,6,7,8-tetrahydro-2-naphthylamine) did not result in an increased yield of **4**, however.

An important structural difference between Cd^{II}₈L₈ **4** and tetrahedra **1**–**3** is that **4** contains four *p*-toluidine residues incorporated into its top and bottom faces, pointing inward. The distances between the methyl groups of these anilines varies from 4 to 8 Å (Figure 2). Based on this observation, we envisioned that aniline residues might be incorporated containing terminal alcohol groups, which could hydrogen bond to each other, and thus stabilize **4** with respect to its tetrahedral congeners **2** and **3**. When 2-(4-aminophenyl)-ethanol was used in place of *p*-toluidine in the system of Scheme 1, 51% of ligand **L** was incorporated into *endo*-Cd^{II}₄L₄ **2**, 13% into *exo*-Cd^{II}₄L₄ **3**, and 36% into Cd^{II}₈L₈ **4** at 16 mM [Cd^{II}]. This aniline thus increased the formation of **4** more than 3-fold. We next investigated solvents that are less disruptive to the formation of hydrogen bonds than acetonitrile. Complexes **2**–**4** were not observed to dissolve in chloroform or dichloromethane. When self-assembly was carried out in a 1:3 mixture of dichloromethane and acetonitrile, however, **4** was the principal product, incorporating approximately 90% of the total **L** (Scheme 1, (iv)).

In conclusion, we have shown how the self-assembly of flexible subcomponent **A** can give rise to diverse product structures, which can coexist because they are nearly isoenergetic. Two of the three Cd^{II}-templated products are tetrahedral, of which only one has a cavity available for guest encapsulation. The third is a new structure type formed by eight ligands and eight metals. Thorough investigation of the

system uncovered the means to favor each assembly over the others. Future work will focus on using similarly flexible ligands, which are reminiscent of biological molecules that have several preferred conformations, with a view to switching between the different functions expressed by these distinct conformations in response to external stimuli, biomimetically.¹⁹

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12955.

Synthetic details, characterization data, NMR and mass spectra (PDF)

X-ray crystallography data for **1** (CCDC 1439852) (CIF)

X-ray crystallography data for **4** (CCDC 1439853) (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*jrn34@cam.ac.uk

Notes

The authors declare no competing financial interest.

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